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PROVISIONAL APPLICATION FOR PATENT COVER SHEET

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This is a request for filing a Provisional Application for Patent under 37 CFR 1.53(c)

Inventor(s) and Residence(s) (city and either state or foreign country):

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Title: **Method and System for Applying Coatings onto the Interior Surfaces of Components**

11 Sheets of specification.
____ Sheets of drawings.

University of Virginia Patent Foundation claims small entity status as a nonprofit organization (37 CFR §§1.27(a)(3) and (c)). The Commissioner is hereby authorized to charge the Small Entity Fee of $80 to **Deposit Account No. 50-0423.**

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This invention was made by an agency of the United States Government or under a contract with an agency of the United States Government. The government has certain rights in the invention.

YES ☒ NO ☐ Grant No. ONR Grant

Dated: January 8, 2004

Respectfully submitted,

By:
Robert J. Decker (Reg. No. 44,056)

Method and System for Applying Coatings onto the Interior Surfaces of Components

BACKGROUND OF THE INVENTION

The useful lifetime of small and medium diameter (about 20 to 40 mm) gun barrels is limited by damage of the interior surfaces resulting from mechanical and thermo-chemical effects related to passing a projectile through the gun bore and subsequent exposure of the interior surface to hot propellant gases. Coatings to protect the interior surfaces of the barrel are therefore frequently employed. Traditionally, the gun barrels have contained chromium coatings that are applied on the interior surface via electroplating. These coatings provide adequate performance; unfortunately hexalavent chrome is created during the electrodeposition process. This material is toxic and difficult to dispose of. Executive Order EO13148 requires the usage reduction of hexavalent chrome (the primary element of electro-deposition) by 50% before the end of 2006. New deposition approaches for wear resistant coatings are therefore desired that retain the high throwing power and affordable cost structure of electroplated chrome but are inherently environmentally safe.

Several other deposition options for protective coatings currently exist. These include approaches such as thermal spraying, chemical vapor deposition (CVD) and the various physical vapor deposition (PVD) approaches. The internal surfaces, however, are hidden from sight making even thickness coating of internal surfaces very difficult or impossible. While high pressure CVD using metal-organic precursors may at first provide a promising approach, non-uniform deposition and vapor toxicity issues plague this approach. Thus, the desired combination of non-line-of-sight coating capability, high deposition uniformity, environmental inertness and compositional flexibility required has been difficult to achieve.

Perhaps the most promising approach is PVD. These approaches are growing in interest for many applications because they are environmentally friendly, allow adequate materials flexibility and enable the deposition of high quality, thin films. In most PVD based processing approaches, however, it is not possible to uniformly coat the interior of hollow tubular substrates without spatially distributed sources (such as cylindrical magnetron sputtering (CMS) where

source targets are inserted into the interior of the part). This arises because the vapor atoms are created in a high vacuum that results in nearly collisionless vapor transport to the substrate. As a result, only regions in the line-of-sight of the vapor source are coated. Even for the cases of thin films deposited with cylindrical magnetron sputtering, deposition rates are relatively low and the vacuum requirements are stringent (< 10^{-4} Pa) so that the cost effectiveness of these approaches in relation to electroplating is in question. In addition, the ability of these processes to deposit coatings into the grooves found in rifled gun barrels is also an issue. Nevertheless, this PVD approach still appears to be one option for coating large diameter gun barrels (> 40 mm). Its application to smaller diameters, however, is not yet clear because of issues related to the stability of the ionization and deposition processes involved. Thus, the advent of a new deposition process that improves upon the economic and the line-of-sight limitations of current PVD approaches (such as CMS) while retaining their many advantages is of interest for applications such as gun barrel coatings and the coating of other tubular substrates.

Other applications that would benefit from such an advancement include wear and corrosion resistant coatings for the interior surfaces of aircraft landing gear components, wear resistant coatings for actuators in suspension control systems used on automobiles, hydraulic and pneumatic actuators, linear electric motors and the internal surfaces of bearings.

BRIEF SUMMARY OF INVENTION

The present invention provides a methodology and system for applying coatings onto, but not limited thereto, the interior surfaces of components. The approach consists of a vapor creation device (for example an electron beam or laser that evaporates a single or multiplicity of solid or liquid sources), a vacuum chamber having a moderate gas pressure (between 0.1 and 1000 Pa) and a inert gas jet having controlled velocity and flow fields. Vapor created from a source is transported into the interior regions of a component using binary collisions between the vapor and gas jet atoms. Under certain process conditions these collisions enable the vapor atoms to scatter onto the interior surfaces of the component and deposit. By using a vertically translatable deflector plate or secondary gas jets the thickness uniformity and microstructure of the coating can be uniquely controlled. The result is the ability to deposit monolithic metals or

alloys, multilayer coatings, functionally graded coatings and nanoscale composite coatings onto interior surfaces. The approach is environmentally friendly and potentially low cost.

BRIEF SUMMARY OF THE DRAWINGS

Figure 1 – Schematic illustration of a DVD coater used for coating the interior of tubing or the like.

Figure 2 – Aluminum coating deposited onto a stationary steel fiber using DVD. Significant NLOS coating was achieved on the backside of the fiber (70% of the frontside). The coating morphology was similar on all regions

Figure 3 -- Schematic illustration showing a) process conditions on the interior of the tube that are set to allow lateral diffusion within the jet and deposition onto the interior surfaces and b) the use of a vertically translating deflector plate that alters the streamlines of the carrier gas jet and promotes the deposition of vapor atoms having a near normal angle of incidence in a deposition zone near the vertical position of the deflector plate.

DETAILED DESCRIPTION OF THE INVENTION

In general, physical vapor deposition processes can be considered as multi-step processes; a) vapor creation, b) vapor transport, c) vapor adatom adsorption and d) assembly on the substrate. Methodologies for the creation of the vapor are many and have been widely researched as has the assembly processes at the substrate. Not until recently have new methodologies that manipulate and control the vapor transport step received significant interest (plasma activation processes altering vapor atom kinetic energy being one exception). These approaches are driven by a need for improved control of the vapor transport processes that enable increased process efficiency, improved composition control and non line-of-sight (NLOS) deposition. These attributes promise to greatly improve the economy of PVD processes and its potential range of applications.

One approach to alter the vapor transport step is the use of binary collisions between vapor atoms and a moving background gas. This is enabled by the use of moderate chamber pressures to control the mean free path between vapor / background gas collisions and trans-sonic gas jets to alter the speed of the gas. The result is that several aspects of the vapor transport step can be beneficially controlled. These include the ability to tailor the spread of a thermally evaporated flux to the size of the desired substrate to increase deposition rates, the ability to deposit materials onto non line-of-sight regions of substrates and the ability to control the intermixing between multiple vapor sources.

Directed vapor deposition (DVD), is an advanced approach based on this innovative concept, **Figure 1**. It provides the technical basis for a flexible, high quality coating process capable of atomistically depositing dense, compositionally controlled coatings onto line-of-sight *and* non line-of-sight (NLOS) regions of components. DVD technology utilizes a trans-sonic gas jet to direct and transport a thermally evaporated vapor cloud onto a substrate. The vapor is deposited with a high materials utilization efficiency resulting in high deposition rates (> 10 μm min^{-1}). Typical operating pressures are in the 1 to 50 Pa range. Thus, only inexpensive mechanical pumping is required. In this pressure regime, collisions between the vapor atoms and the gas jet create a mechanism for transporting the vapor atoms into regions of components that are not in the line-of-sight of the source and then scattering them onto these surfaces to result in NLOS deposition.

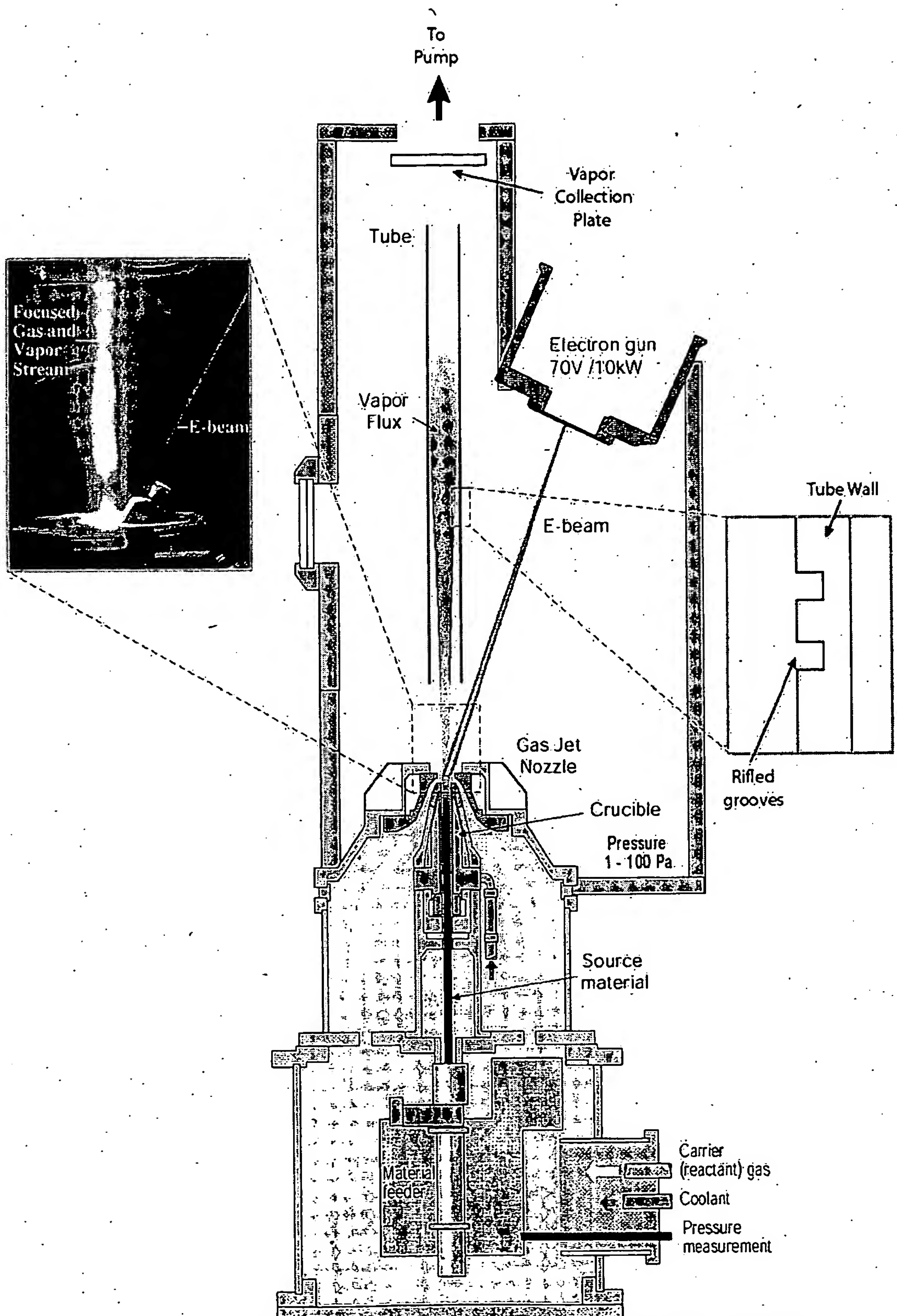


Figure 1 – Schematic illustration of a DVD coater used for coating the interior of small diameter (20 to 40mm) tubing

Additional capabilities include the use of high frequency e-beam scanning (100 kHz) that allows multiple source rods to be simultaneously evaporated. By using the binary collisions between the gas jet atoms and the vapor, the fluxes are intermixed enabling the composition of the vapor flux (and thus, the coating) to be uniquely controlled. Multilayer or functionally graded coatings are created by adding a given e-beam dwell time onto two or more of the source materials.

To enable dense coatings of high melting point materials at low substrate temperatures hollow cathode plasma activation can also successfully be used in this process environment. This enables a large percentage of all gas and vapor species to be ionized. The ions can then be accelerated towards the coating surface by an applied electrical potential increasing the velocity (and thus the kinetic energy) of the ions allowing the coating density to be increased.

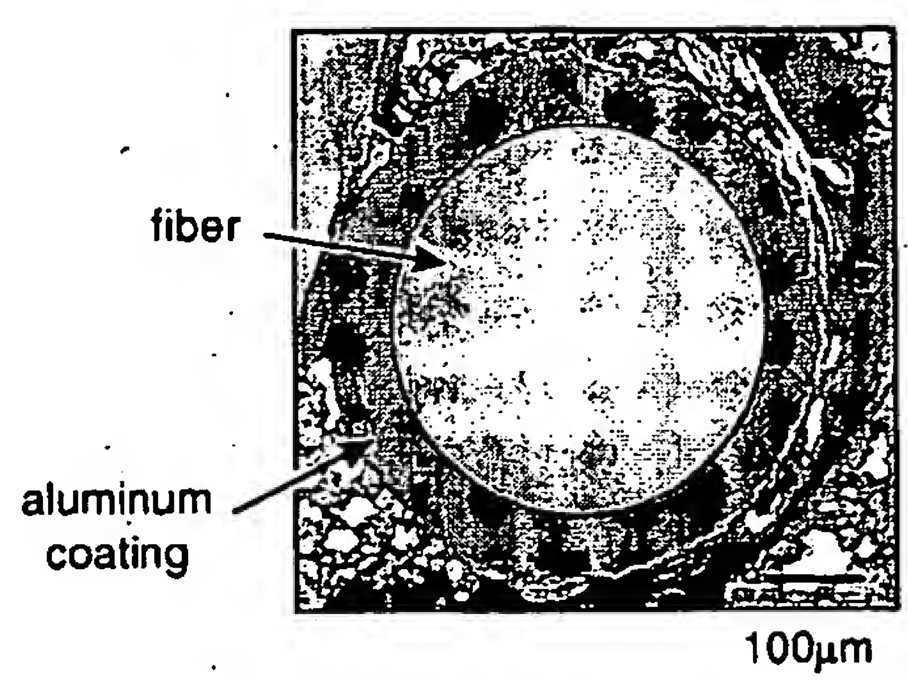


Figure 2 – Aluminum coating deposited onto a stationary steel fiber using DVD. Significant NLOS coating was achieved on the backside of the fiber (70% of the frontside). The coating morphology was similar on all regions

When using the DVD approach as a means for obtaining enhanced NLOS coating (such as the case for gun barrel coatings), chamber pressures are carefully chosen to allow some binary collisions between the vapor and gas jet atoms to enable a mechanism to control the trajectories of the vapor atoms, but not three body collisions that enable the nucleation of clusters that can detrimentally affect the coating microstructure. Significant NLOS coating has been observed when coating stationary fiber substrates since the gas jet could be used to transport vapor atoms to the backside of the fiber where they could deposit via scattering, **Figure 2.**

This basic process can be extended to allow coating onto the interior surfaces of tubes. Vapor atoms are created using e-gun evaporation and then focused into the tube using a carrier

gas where they deposit on the interior via lateral diffusion within the gas flow, **Figure 3(a)**. In this case, the average carrier gas trajectories are parallel to the walls of the tube. However, when the process conditions are set so that vapor atoms have a "random walk" aspect to their motion the vapor atoms only generally follow the carrier gas trajectories and can laterally diffuse via binary collisions.

Control of the vapor atom diffusion process is critical to the successful deposition of high quality, uniform coatings on the interior of these parts and is accomplished by the control of the speed and density of the background gas. When the Knudsen number (i.e. the ratio between the mean free path in a flow to the characteristic length of a body immersed in the flow) for the carrier gas is ~1 and the gas speed is highly subsonic (< 200 m/s) the vapor atoms can diffuse laterally and impact the tube walls with an incidence angle near the substrate normal. Since the carrier gas speed affects the lateral diffusion distances, gradients in the speed from the tube entrance to the tube exit can be used to control the coating thickness uniformity throughout the length of the tube. Recent work has also shown that control of the gas speed can also prevent vapor atoms from impacting the surface at oblique angle. Oblique impacts promote shadowing mechanisms that lead to unwanted porosity in the coatings and thus need to be prevented.

Other methodologies also exist for controlling the coating thickness uniformity and angle of incidence distribution at the interior surfaces. For example when coating the interior of a tube, process conditions that result in a gradual thickness gradient from the entrance of the gas/vapor flux to the exit would benefit from simply reversing the entrance and exit (by rotating the tube 180°) during the deposition process. Another example is the use of a vertically translatable deflector plate, **Figure 3b**. This could consist of a cone shaped deflector with small exit points for an argon clearing gas. The deflector would favorably alter the carrier gas trajectories to promote vapor atom deposition in a "deposition zone". By translating the deflector vertically the thickness uniformity could be precisely engineered. The argon clearing gas is used to prevent deposition onto the deflector plate and improve the process efficiency. A translatable screen or mask would be used to prevent deposition outside of the "deposition zone". This could be a telescoping design or be made of a flexible material so that the mask would not interfere with the evaporation processes occurring at the source. The uses of pulsed secondary jets moving in the opposition direction of the vapor flux or deflector plates having other geometries are additional

options.

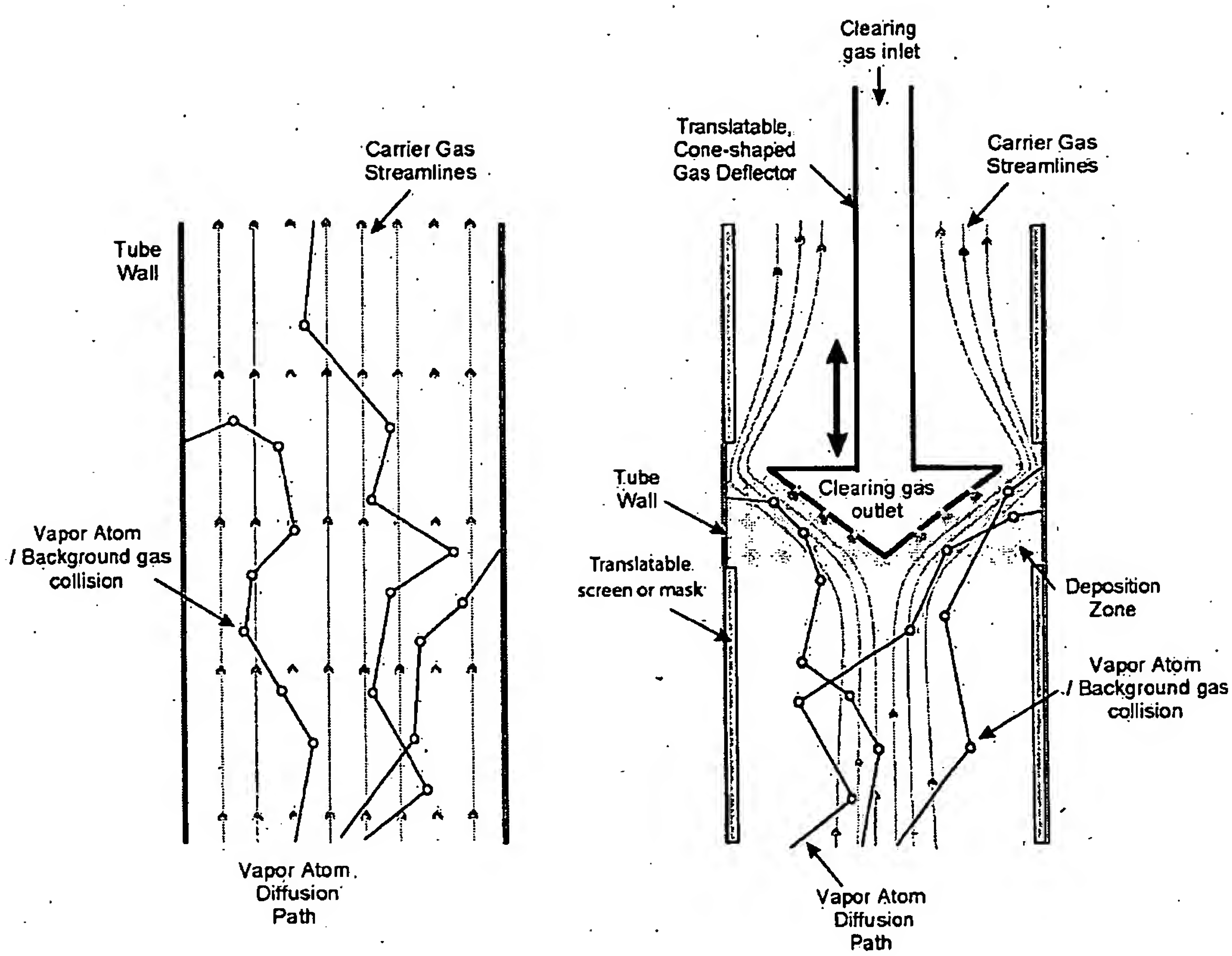


Figure 3 – Schematic illustration showing a) process conditions on the interior of the tube that are set to allow lateral diffusion within the jet and deposition onto the interior surfaces and b) the use of a vertically translating deflector plate that alters the streamlines of the carrier gas jet and promotes the deposition of vapor atoms having a near normal angle of incidence in a deposition zone near the vertical position of the deflector plate.

PUBLICATIONS AND REFERENCECES

The following references, publications, applications, and patents are hereby incorporated by reference herein in their entirety:

International Application No. PCT/US03/12920, filed April 25, 2003, filed April 25, 2003, entitled "Apparatus and Method for Uniform Line of Sight and Non-Line of Sight Coating at High Rate;"

D.D. Hass, Y. Marciano and H.N.G. Wadley, "Physical Vapor Deposition on Cylindrical Substrates", *Surf. Coat. and Technol.* (2003) in press;

International Application No. PCT/US03/37485, filed November 21, 2003, entitled "Bond Coat for a Thermal Barrier Coating System and Related Method thereof;"

International Application No. PCT/US03/36035, filed November 12, 2003, entitled "Extremely Strain Tolerant Thermal Protection Coating and Related Method and Apparatus Thereof,"

International Application No. PCT/US03/23111, filed July 24, 2003, entitled " Method and Apparatus for Dispersion Strengthened Bond Coats for Thermal Barrier Coatings;"

International Application No. PCT/US02/28654, filed September 10, 2002, entitled " Method and Apparatus for Application of Metallic Alloy Coatings;"

U.S. Pat. No. 5,534,314, filed August 31, 1994, entitled "Directed Vapor Deposition of Electron Beam Evaporant;"

U.S. Pat. No. 5,736,073, filed July 8, 1996, entitled "Production of Nanometer Particles by Directed Vapor Deposition of Electron Beam Evaporant;"

U.S. Pat No. 6,478,931 B1, filed August 7, 2000, entitled "Apparatus and Method for Intra-layer Modulation of the Material Deposition and Assist Beam and the Multilayer Structure Produced There from," and corresponding Divisional U.S. Application No. 10/246,018, filed September 18, 2002;

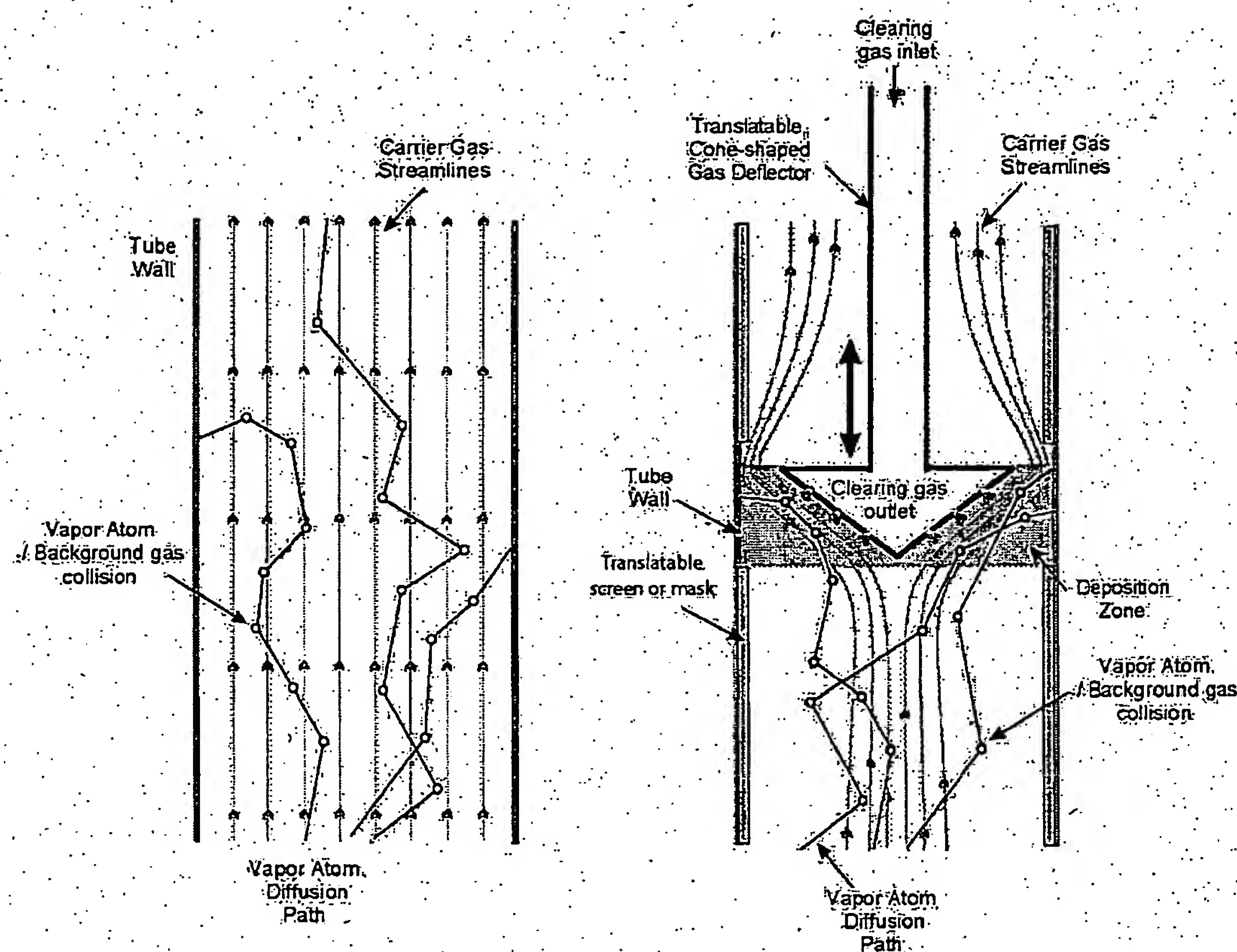
International Application No. PCT/US01/16693, filed May 23, 2001 entitled "A process and Apparatus for Plasma Activated Deposition in a Vacuum," and corresponding U.S. Application No. 10/297,347, filed Nov. 11, 2002; and

International Application No. PCT/US02/13639, filed April 30, 2002 entitled "Method and Apparatus for Efficient Application of Substrate Coating."

In summary, the present invention coating may be implemented for, but not limited thereto, the following products and systems:

- Coatings for military gun barrels and rifle barrels
- Coatings for aircraft landing gear
- Coatings for actuators in suspension control systems
- Wear and corrosion resistant coatings for the interior surfaces of aircraft landing gear components
- Wear resistant coatings for actuators in suspension control systems used on automobiles,
- Hydraulic and pneumatic actuators
- Linear electric motors and the internal surfaces of bearings

options.



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